Photocatalytic decomposition of gaseous formaldehyde using TiO_2 , $\text{SiO}_2 - \text{TiO}_2$ and $\text{Pt} - \text{TiO}_2$

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ABSTRACT. In this study, in order to improve the photocatalytic decomposition activities of formaldehyde, TiO_2 catalyst modified with SiO_2 substitution and metal (Pt, Cu and Fe) impregnation, were tested. In case of TiO_2 substituted by SiO_2 , the optimal catalytic activity was found at the mole ratio of 2 : 8. Among the metal impregnated TiO_2 , the Pt impregnated TiO_2 showed the best activity even better than that of P-25 which is widely used in commercial application. However, Cu and Fe impregnated TiO_2 showed the reverse effect. In the case of SiO_2 substituted TiO_2 the observed values of photoluminescence spectroscopy were quite proportional to the photocatalytic activities depending upon the mole ratio of SiO_2 to TiO_2 . However, for the samples of metal impregnated TiO_2 , the reverse relationships were found. In UV-visible spectra for metal impregnated TiO_2 , the transmittance value was reduced depending upon the loading of metals. The enhanced photocatalytic activity for high metal loading on TiO_2 might be associated with the high concentration of excited electron that was monitored through UV-visible spectra.

1. INTRODUCTION

The role of photocatalyst is same with general catalyst in that it promotes the reaction by lowering the activation energy. According to the several article review [1-3], it is essential to suppress the recombination process and to increase the lifetime of separated electron-hole pairs for achievement of high photocatalytic activity, so that fast electron transfer occur from the surface on TiO_2 to adsorbed intermediates. Many researchers have reported that the anatase phase of titania is much more active than rutile one. B. Ohtani *et al.* [4] reported that the anatase phase exists mainly below 773 K, a lower temperature zone. However, if TiO_2 is calcined in this temperature zone, the number of bulk defects that provides site for the recombination of photo-excited electrons would also decreased.

However, if calcination temperature is over 773 K, anatase phase of titania transfer to rutile one and surface area reduce. Also, that makes the photocatalytic activity lower down. So it is necessary to lower the bulk defects and to suppress the transformation of anatase phase to rutile one. Xianzhi Fu *et al.* [5] and E. Obuchi *et al.* [6] have reported that silica substitution to titania enhances the thermal stability and results in repression of the transformation of anatase phase to rutile one. Another method to promote photocatalytic activity is lowering the band gap energy to use the light source which is near visible light or

suppression of the recombination of separated electron-hole pairs which diffuse to catalyst surface. From the view point of Anders Hagfeldt *et al.* [7] and M. Anpo *et al.* [8], doping of transition or precious metal to TiO_2 could function as a trap of recombination of photo excited electron-hole pairs.

M. M. Rahmann *et al.* [9] reported that UV-visible transmittance pattern of TiO_2 could be an index of band gap energy. Also, a photoluminescence spectroscopy, as well as a UV-visible transmittance spectroscopy might be a useful tool to confirm the excited electron-hole pairs as the report of M. Anpo *et al.* [10]. By applying these optical characterization methods, the certain correlations between the photocatalytic activities and the optical properties of those catalysts by using a UV-visible spectroscopy and a photoluminescence spectroscopy were tried and discussed.

2. EXPERIMENTAL

Pure TiO_2 and $\text{SiO}_2 - \text{TiO}_2$ catalysts were prepared by sol-gel method [11]. The mole ratio of $\text{SiO}_2 : \text{TiO}_2$ was 5 : 5, 2 : 8 and 1 : 9, respectively. Also, to prepare metal- TiO_2 catalyst, metal (Pt, Cu and Fe) was impregnated to pure TiO_2 and each metal loading amounts were 3 wt%, 5 wt% and 10 wt%. Then, the prepared catalysts were coated on quartz plate to be the coating depth of 1-2 micro meter. As shown in Figure 1, the apparatus was manufactured to test the activity of prepared catalysts for the photodecomposition of formaldehyde 100 ppm initial concentration and 15 W UV-A lamp was used as a light source.

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Figure 1. Photocatalytic activity test apparatus.

3. RESULTS AND DISCUSSION

In case of SiO_2 - TiO_2 catalysts, as shown in Figure 2, optimal catalytic activity was found at the mole ratio of 2 : 8. Figure 3 shows that the pure TiO_2 catalyst prepared by sol-gel method had only rutile phase when calcined at 973 K. However, in case of SiO_2 - TiO_2 , we could find the anatase phase from XRD results though its crystallinity decrease. The benefit of SiO_2 substitution into TiO_2 comes with the restriction of excess phase transition from anatase phase to rutile one and that enhances the thermal stability during the calcination step in catalyst preparation process. Also, from the result that there is an optimal SiO_2 - TiO_2 ratio, it might be thought the excess substitution of SiO_2 into TiO_2 frame prevents TiO_2 from generating photo excited electron-hole pairs, which means that photocatalytic activity could be lowered [12].

Among metal impregnated TiO_2 catalysts, Pt- TiO_2 exhibited the best photocatalytic activity which was even higher than that of P-25 which is widely used in commercial application. Especially it showed the rapid

Figure 2. Photocatalytic activities with SiO_2 - TiO_2 ratio. Figure 3. XRD pattern of pure TiO_2 and SiO_2 - TiO_2 calcined at 973 K.

increase of reaction rate at initial step mainly because it functioned as a trap of excited electrons and consequently retards the recombination step in photocatalytic reaction cycle.

However, as shown in Figure 4, Fe and Cu showed the similar activity performance at initial step but those changed worse than P-25 as reaction proceeded. This was understood that those impregnated metals function as a trap at initial stage as similar to Pt but it changed into the center for recombination as photocatalytic reaction proceeded as reported by José A. Navío *et al.* [13].

Photocatalytic activities of Pt- TiO_2 with different loading amount were shown in Figure 5. The more metal loading amount increase, the more rapidly photocatalytic decomposition activities increase. This suggested that the more there are Pt, which performs as a trap

Figure 4. Photocatalytic activities with various metal impregnations.

Figure 5. Photocatalytic activities with Pt loading amounts.

of excited electron, on TiO_2 surface, the more separated electron-hole pairs, which enhance photocatalytic activity.

In case of SiO_2 substitution for TiO_2 at the ratio of 2 : 8, the photoluminescence emission intensity was the largest as shown in Figure 6. Also, Figure 7 shows that the observed values of photoluminescence spectroscopy were quite proportional to the photocatalytic activities depending upon the changes in SiO_2 to TiO_2 mole ratio. It could be thought that the more photo excited electron-hole pairs were generated, the more photocatalytic activities increase. For SiO_2 – TiO_2 catalysts, the maximum photoluminescence emission spectra shift slightly into longer wavelength region as proportional to photocatalytic activities, and that means a decrease of the band gap energy, due to substitution incorporation of SiO_2 into TiO_2 lattice.

Also, photoluminescence spectroscopy measurements were performed to measure the amount of photo excited electron-hole pairs depending upon different

Figure 6. Photoluminescence spectra for pure TiO_2 and SiO_2 – TiO_2 .

Figure 7. The relationship between activity and photoluminescence emission value.

metal impregnation amount (3, 5 and 10 wt%), and to investigate the relationship with photocatalytic activities. In Figure 8, the photoluminescence emission value with different Pt loading amount were shown. Also photoluminescence emission pattern of Cu– and Fe– TiO_2 showed similar trends to that of Pt– TiO_2 .

The photoluminescence emission patterns of metal impregnated TiO_2 catalysts were different from those of SiO_2 – TiO_2 catalysts.

In case of SiO_2 – TiO_2 catalysts, photoluminescence emission, which were radiative recombination of excited electrons, are proportional to electron-hole pairs. However, for metal impregnated catalysts, the increase of the surface Ti^{3+} , which results in the increase of non-radiative recombination (relatively it decrease radiative recombination), might cause to enhance photocatalytic activity [14]. When metal was impregnated to

Figure 8. Photoluminescence emission spectra with Pt loading amounts.

Figure 9. Photoluminescence emission spectra with metal impregnated catalysts.

TiO₂, photoluminescence emission value decrease with increasing metal loading amount as shown in Figure 8. Regarding to correlation with activity, it could be found that the smaller the photoluminescence emission value, the higher the photocatalytic activity could be observed as shown in Figure 4 and Figure 9.

In UV-visible spectra for metal impregnated TiO₂, the meaningful difference in peaks depending upon the kinds of metal and metal loading could be observed below the wave number of 230 nm as shown in Figure 10. That was interpreted as the absorption of light due to the excited electrons from valence band to conduction band in TiO₂. Obviously, the transmittance value was reduced depending upon the loading of metals. The enhanced photocatalytic activity for high metal loading on TiO₂ might be associated with the high concentration of excited electrons that were monitored through UV-visible spectra.

The promotion of photocatalytic activity with the loading amounts in Pt-TiO₂ as shown in Figure 11 might be caused by the increase of excited electron

Figure 10. UV-visible transmittance spectra with Pt loading amounts.

Figure 11. The relationship between conversion and UV-visible transmittance.

amounts. Therefore UV transmittance value is reciprocally proportional to metal impregnation amount and photocatalytic activity.

4. CONCLUSIONS

In case of TiO₂ substituted by SiO₂, the optimal catalytic activity was found at the mole ratio of 2 : 8. The substitution of SiO₂ into TiO₂ comes to restrict the excess phase transition from anatase phase to rutile one and that enhances the thermal stability during the calcination step in catalyst preparation process. The observed values of photoluminescence spectra for SiO₂-TiO₂ were quite proportional to the photocatalytic activities depending upon the mole ratio of SiO₂ to TiO₂.

The photocatalytic activity on Pt-TiO₂ showed excellent conversion (over 95%). It could be suggested that the impregnated Pt metal functions as a trap collecting the excited electrons temporarily and consequently it retarded the speed of recombination between electrons and holes on TiO₂. In UV-visible spectra for metal impregnated TiO₂, the transmittance value was reduced depending upon the loading of metals. Also, photoluminescence emission value decrease with increasing metal loading amount. Regarding correlations with activity, it could be found that the smaller the photoluminescence emission value, the higher the photocatalytic activity could be observed. It might be considered as another proof that the better photo absorption has, the increased photocatalytic activity could be obtained.

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